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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> METHOD FOR RECOVERING AN ORGANIC COMPOUND FROM SOLUTIONS  <b>(57) Abstract</b>  The invention relates to a method for recovering a crystallisable organic compound from solutions containing said compound. In accordance with the method, the compound is crystallized substantially by way of nucleation from a solution having high viscosity and high super-saturation in respect of the compound to be recovered, and the formed crystals are recovered.		

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## Method for recovering an organic compound from solutions

The present invention relates to a method by which a crystallisable organic compound can be recovered from solutions containing said compound. In particular, the invention relates to a method by which water-soluble organic compounds can be crystallized from supersaturated aqueous solutions having very high viscosity and then recovered from the solutions.

The two principal steps of crystallization are the formation of crystal seeds (nucleation) and crystal growth. In most industrial processes, crystallization is primarily based on crystal growth. The state of the art with respect to crystallization is represented for example by Mathlouthi, M. and Reiser, P. (ed.), *Sucrose, Properties and Applications*, Blackie Academic & Professional, Suffolk, Great Britain, 1995, p. 49 ff. This disclosure explains the crystallization mechanism with respect to both nucleation and crystal growth. With regard to the industrial crystallization of sucrose, this publication states, for instance, that one must avoid concentrating the solution up to the nucleation zone, i.e. the zone whereat spontaneous nuclei formation readily occurs (p. 58); one must avoid the creation of an uncontrolled number of seeds (p. 59); the crystals to mother liquor ratio cannot be increased beyond a certain value (pp. 59-60); and crystallization should be carried out in the metastable zone not too close to the nucleation zone and the saturation curve (pp. 60-61, and pp. 63-64). The metastable zone is the zone where spontaneous crystal formation will occur only if crystals are present. It is emphasized that in this zone no new crystals are formed in the absence of seeds. Furthermore, according to this publication (cf. e.g. pp. 57 and 58) impurities decrease the crystal growth rate and may even block the growth completely.

With an increase in supersaturation and a decrease in the temperature of the solution, the viscosity of the solution also increases, thus slowing down and eventually completely blocking diffusion of the molecules through the liquid layer surrounding the crystals or crystal nuclei to the crystal surface, and hence prior art processes based on crystal growth are no longer possible. In accordance with the prior art, high viscosity has also been regarded as a downright impediment to the separation of crystals from the mother liquor.

In respect of sucrose crystallization, these problems have also been discussed in the above publication Mathlouthi, M. and Reiser, P. (ed.), *Sucrose, Properties and Applications*.

The methods for recovering sucrose employed in the sugar industry typically comprise three successive crystallization steps. In the last step, which is known as 'C' crystallization, the sucrose content of the starting material syrup is about 73-75% on dry substance; this crystallization method is slow and difficult, and yet the sucrose purity (% of sucrose on dry substance) of the run-off, i.e. molasses, obtained therefrom is still typically as high as about 58%. There are several methods by which it is sought to improve the sucrose yield, i.e. to diminish the sucrose purity of molasses. Such methods include the Quentin and Steffen methods and the molasses fractionation methods of the type described in Finnish Patent 77 845 (Suomen Sokeri Oy; Heikkilä, Melaja, Millner, Virtanen; corresponds to international published application WO 81/02420). Such fractionation methods enable a fraction enriched with betaine wherefrom betaine can be recovered to be obtained from molasses.

In conventional methods, it has only been possible to crystallize xylose if the xylose purity has been at least about 70% by weight on dry substance. In that connection, it has been necessary to first purify the xylose-containing solution obtained for example as a result of hydrolysis of vegetable-derived material to the required degree of purity by various ultrafiltration, ion exchange, decolouring, ion exclusion or chromatographic separation methods or combinations of these; furthermore, auxiliary solvents diminishing the solubility of xylose have been employed to crystallize xylose.

The above xylose separation, purification and crystallization methods have been described for instance in U.S. Patents 4 631 129 (Heikkilä, H.; Suomen Sokeri Oy), 4 075 406 (Melaja, A. J. & Hämäläinen, L.; Suomen Sokeri Oy), 5 084 104 (Heikkilä, H. & Hyöky, G.; Cultor, Ltd) and 4 168 988 (Riehm, T. & Hofenk, G; Institut voor Bewaring en Verwerking van Landbouwprodukten) and the publications referred to therein.

When xylose is prepared by hydrolyzation of xylan, an alternative to the above methods is to purify the xylan prior to its hydrolyzation into xylose to obtain a xylose solution of sufficient purity. Also this procedure is very complex and cumbersome, as will be apparent from Browning, B.L., *Methods of wood chemistry*, II, Interscience Publishers, New York, 1967, and Fry, S.C., *The growing plant cell wall: chemical and metabolic analysis*, Longman Scientific & Technical, England, 1988.

In accordance with German Offenlegungsschrift 1 643 940 (Eickenmeyer, R. & Scholler, H.), crystalline xylose is recovered from a hydrolysate of pentosan- and cellulose-containing natural substances by crystallization from a syrup containing at least about 70% of xylose. The syrup is introduced into a crystallizer at 60-

70 °C, and a crystal mass containing 15-33% of xylose on the amount of xylose supplied to the crystallizer is taken from the crystallizer at 48-52 °C. Crystals are separated from this crystal mass by centrifugation, and the mother liquor, the amount of which is 300-100% of the fresh syrup supplied to the system, is combined with the starting material hydrolysate. The resultant mixture of mother liquor and hydrolysate is treated in a cation exchanger and an anion exchanger, and after a subsequent decolouring treatment the mixture is evaporated in order to obtain a syrup to be supplied to the crystallizer. In addition to cumbersome purification treatments, the method thus comprises very extensive recycling. In accordance with this publication, the small amount of xylose obtained in one crystallization (the small yield as compared with the xylose supplied to the crystallizer) is due to fact that when the temperature falls below about 48 °C, the crystallization rate will be very small on account of the fact that the viscosity of the solution substantially increases when the temperature drops.

U.S. Patent 3 981 739 (Dmitrovsky et al.; Amstar Corporation) relates to a method of continuously crystallizing sugars (sucrose, dextrose, fructose, lactose, carbohydrates). The method involves controlled growth of crystals in two-stage evaporative crystallization starting from seed crystals of small size. The crystals in the first stage are substantially larger than the seed crystals, and crystals of increased size are produced in the second stage.

U.S. Patent 4 199 373 (Dwivedi et al.; Chemicassa GmbH) relates to a process for manufacturing free-flowing mixtures of fructose and glucose avoiding the disadvantages of earlier processes (such as the need of sophisticated machinery and careful control, high energy

costs and low yield). The process is a solidification method; it includes no separation of crystals and mother liquor. A highly concentrated solution is seeded and permitted to stand (thus allowing crystallization to take place) at a specific temperature and relative humidity, recovered, dried and ground. Too low a concentration results in a pasty mass, too high a concentration results in a glassy mixture. It is essential that the surrounding air has a relative humidity below 50% and a temperature between 50-90 °F (10-32 °C).

Other total solidification processes are disclosed, for example, in U.S. Patent Nos. 4 297 146 (Mise et al.; CPC International Inc.), 4 595 418 (Yoshino; Sanwa Kosan Kabushiki Kaisha) and 4 640 717 (Shukla et al.; Tate & Lyle Public Limited Company).

U.S. Patent 4 634 472 (Niekamp et al.; A.E. Staley Manufacturing Company) provides a process for manufacturing an enriched fructose syrup. In this process, a feed syrup (75-89% dry solids concentration) temperature is established appropriate for crystallization of glucose. It is well known in the art that the easy crystallization of glucose, even at low purity, is often a problem, as for instance in the case of honey (typical solid concentration 81-85%, about 40% of glucose and about 30% fructose on dry solids). It is also known (Harold E. Horn, "Dextrose: An Alternative to Sucrose in Panned Confections", *The Manufacturing Confectioner* for 1977) that glucose crystallization is increasingly inhibited at viscosities of 10,000-100,000 cP (10-100 Pas). Calculated from Example 1 of U.S. Patent 4 634 472, the crystallization viscosity is only about 2000 cP, which represents a very low viscosity solution. No water can be used as a diluent in the process according to U.S. Patent 4 634 472 (column 5, lines 20-25), since the crystals would dissolve.



U.S. Patent 4 816 079 (Ahrens et al.; Fried Krupp GmbH) relates to a process for continuous crystallization of dextrose monohydrate. The process is, in principle, a traditional cooling crystallization method based on crystal growth. Part of the feeding syrup is subjected to a shearing process for a period of 0.01-2 seconds to initiate nucleation for producing seed crystals for the process.

Accordingly, there is a need for an economical and efficient process to achieve a high recovery of crystalline product from a solution containing same, especially a source, having lower levels of crystallizable product than are directly processable under comparable conditions to achieve the same yield.

It is then a principal object of the invention to achieve an improvement in overall yield of recovered crystallizable organic compounds from solutions containing same.

It is a further object to economically utilize in such processes material streams impure in crystallizable organic compounds contained therein.

It is also an object to employ run-off or recycle stream from industrial processes containing crystallizable organic compounds as a source for the efficient recovery of such compounds in good yield.

It has now been found that crystallisable organic compounds that form solutions having high viscosity can be recovered from such solutions by crystallization when the supersaturation value is sufficiently high and when the crystallization is performed substantially by way of nucleation, i.e. in such a way that crystal growth is not significant in the process. Thus the compounds can be crystallized even from comparatively impure solutions wherefrom they could not previously be crystallized. In the context of the present description and claims, high

viscosity denotes a viscosity at which crystal growth is substantially retarded. Specifically, in the present invention a solution is considered as having a high viscosity if its viscosity is in the range from about  $10^5$  cP to about  $10^6$  cP (100-1000 Pas).

The invention thus affords a method for recovering a crystallisable organic compound from solutions containing said compound, being characterized in that the compound is crystallized substantially by way of nucleation from a solution having high viscosity and high supersaturation in respect of the compound to be recovered, and the formed crystals are recovered.

The crystallization of the invention is preferably carried out beyond the metastable zone, i.e., employing the terminology of Mathlouthi, M. and Reiser, P. (ed.), *Sucrose, Properties and Application* for instance, in the nucleation zone which in accordance with said publication should be avoided in the crystallization of sucrose, for example.

In the method of the invention, nucleation is enhanced by effective stirring, thus enabling the nucleation to occur spontaneously. The stirring is effected as vigorously as the high viscosity permits to achieve efficient continuous intermixing of portions of crystallization mass into and from the higher shear zones in which nucleation is favored so to maximize crystallization through the mass. In this way the solidification of the crystallization mass is avoided, and the nuclei are able to develop crystal shape and to grow until crystal growth is blocked, whereby the highest yields are realized. To induce nucleation, seed crystals may also be added to the supersaturated solution. The final crystal size is typically limited to about 10-120  $\mu\text{m}$ . The improvement in recovery of the crystallizable compound achieved by the present invention is fundamentally based

on a nucleation mechanism in very viscous solutions under continuous intermixing by which overall crystallization yield is maximized.

After nucleation has started, the high viscosity of the mother liquor of the suspension (i.e. crystallization mass) obtained substantially prevents crystal growth and discharge of the supersaturation state; yet nucleation continues on account of effective stirring. During the first period of the nucleation process of the present invention, the suspension is cooled down to reach and maintain a high supersaturation of the mother liquor. Thereafter, the temperature of the crystallization mass and concentration of total solids are practically constant. The supersaturation of the mother liquor is maintained high during the entire crystallization phase, i.e., the system is continually maintained substantially above the metastable range.

In the present description and claims, supersaturation of the solution denotes its apparent supersaturation in respect of the organic compound to be recovered, i.e. the dimensionless ratio of the measured content and solubility of said compound, which is calculated from the equation:

$$S = \frac{\text{content of compound in sample solution}}{\text{solubility of compound at temperature of sample solution}}$$

wherein  $s$  is supersaturation, and the unit of measurement for the content and solubility of the compound is g of pure compound/100 g of solvent. Also the terms "supersaturated" and "supersaturation" singly refer to the saturation of the solution in respect of the compound to be recovered. The purity of the substance denotes its percentage in the dry substance.

High supersaturation denotes a supersaturation at which nucleation process is dominant and crystal growth is inhibited. Typically, in the present invention a solution is considered having a high supersaturation when  $s$  is between 1.4 and 4.

It is known in the prior art that a relatively high supersaturation is needed for nucleation, and this is most effectively maintained at low viscosity by applying strong mixing. If nucleation as such is preferred, then obvious operation conditions would be a relatively low viscosity and vigorous mixing. Contrary to that, high viscosities are used in the present invention, whereby superior recovery of the crystallizable compound can be obtained.

In accordance with the prior art, also the problems involved in the separation of a small-crystal product from a mother liquor at high viscosity of the crystallization mass have hindered the industrial application of crystallization based primarily on nucleation. Strong nucleation (spontaneous crystal formation) is therefore typically regarded as a failure in traditional crystallization processes. In accordance with an additional aspect of the invention, the small-crystal product produced in the nucleation can nonetheless be separated from the crystallization mass when the viscosity of the crystallization mass is decreased immediately before the recovery of crystals or in connection with the recovery of crystals. Viscosity can be decreased for example by heating the crystal mass and/or diluting it either with a dilute starting material solution or the solvent contained therein. Also addition of another solvent in which the crystals do not substantially dissolve is possible; for example in the recovery of sucrose, glycerol could be used as such a solvent.

A special embodiment of the invention is the recovery by filtration of a small-crystal fraction obtained by nucleation.

5 In typical prior art crystallization processes, considerable amounts of the product are lost in the final mother liquors. The present invention leads to remarkable additions in the recovery of the desired product from the mother liquor. Recovered material can be further refined by traditional crystallization processes. Typical improvement achieved by the present  
10 invention in total yield is 5-30% or even more compared with prior art processes, and total yields of up to 80% can be obtained from aqueous solutions where traditional crystallization is ineffective.

15 The method of the invention is particularly suitable for the recovery of carbohydrates, which preferably are readily crystallizable such as aldoses and alditols, for example sugars and sugar alcohols, and hydroxy and amino acids and betaine from aqueous solutions thereof.  
20 The term "aqueous solution" as employed herein denotes a medium wherein the crystallizable compound is initially dissolved thereby providing a single, homogeneous continuous phase containing a sufficient concentration of the crystallizable compounds such that when the solution  
25 is concentrated to its supersaturated state nucleation readily occurs. It is understood that the aqueous solution may comprise other substances miscible therewith either as impurities in the feed or as adjuvants to facilitate further processing.

30 Since the method is capable of recovering these compounds even from substantially impure solutions, it is suitable for use in the recovery of organic compounds from biomass-derived aqueous solutions. Such solutions include molasses and vinasse, biomass hydrolysates or  
35 parts thereof or concentrates obtained therefrom, such

as cooking liquors of the pulp industry. Such aqueous solutions also include run-offs (mother liquors wherefrom crystals have been separated) obtained in the present-day industrial crystallization processes in which the purity of the compound to be recovered in the raw material solution is comparatively high and the impurities are discharged in the run-off. Furthermore, this method is suitable for the recovery of products prepared by way of fermentation, such as gluconates, glutamates and lactic acid, from the fermentation solutions thereof.

The method of the invention is suitable for the recovery of for example the following compounds: xylose, mannose, xylitol, mannitol, lactose, lactitol, sucrose, glucose, fructose, maltose, maltitol, isomaltose, isomaltulose, lactulose,  $\alpha$ -D-glucopyranocycl(1-6)mannitol,  $\alpha$ -D-glucopyranocycl(1-6)sorbitol,  $\beta$ -cyclodextrin, itaconic acid, citric acid, betaine, inositol, 1,4-anhydroglucitol.

The method of the invention is particularly advantageous in cases where the crystallisable substance has been recovered from solutions by crystallization by known methods to the extent that is technically possible or economically feasible. In other words, the method is particularly advantageous in recovering a crystallisable substance from solutions having low purity of the substance.

The solution from which the organic compound is recovered by the method of the invention is first brought to a state of sufficient supersaturation to produce nucleation. Typically, this is achieved by concentration and/or cooling. A preferred concentration method is evaporation under subatmospheric pressure. The solution can be concentrated for example to a dry substance content of 75-98% by weight; the preferred dry

substance content is dependent on the solution to be treated and can be 82-95% by weight, for instance. The degree of supersaturation is maximized under the conditions obtainable within the limit of workable viscosity.

To produce crystals from a supersaturated solution, cooling is most often employed, the quality and crystallization propensity of the solution to be treated affecting the cooling time and rate. In the nucleating step the rate of cooling of the supersaturated solution and the application of working energy to the mixing process is interrelated in practice to avoid the solidification of the crystallization mass and to limit crystal growth to provide crystals generally in the range of not greater than 10-100  $\mu\text{m}$ , for example, while promoting further nucleation of the crystallization mass. In general too high a local shear rate without effective intermixing can lead to the solidification of the crystallization mass and should be avoided. At a given viscosity and power input, crystal size distribution is controlled by the cooling rate. Higher purity sources may be cooled more quickly, whereas sources with greater impurities or natural inhibitors may require a slower rate.

Prior to the initiation of the cooling, finely ground seed crystals of the compound to be recovered are preferably added to the solution; the crystallization can, however, also be initiated by spontaneous seeding. The term "full seeding" employed hereinbelow in connection with seeding is commonly known in the art (see "Beet-Sugar Technology", 3rd Edition, edited by R.A. McGinnis (1982) pp. 371-481) and is calculated from the size of seed crystals, the crystal size in the desired end product, and the yield, provided that the number of crystals does not change.

The solution brought to the state of supersaturation required by nucleation, and the suspension formed by such a solution and the crystals contained therein, will also be termed crystallization mass in the following.

The method of the invention is particularly advantageous and is representatively described in the recovery of xylose from solutions having a comparatively low xylose content on dry substance, i.e. about 30-50% by weight on dissolved dry substance. In that case, the separation processes involved in the prior art processes can be considerably lessened or totally eliminated, and the use of auxiliary solvents can also be eliminated, thus making the method essentially more inexpensive than the prior art methods, and xylose can be recovered in the form of a crystalline product from xylose solutions that are difficult to purify for example by chromatographic separation which, therefore, does not yield such xylose purities as are required in the prior art crystallization methods. In particular, the object of the invention is such a method for recovery of xylose from hydrolysis products of biomass, which may also be xylose-containing by-product fractions obtained in the wood processing industry, such as sulphite cooking liquor or a part thereof or a concentrate obtained therefrom, for instance a concentrate chromatographically produced from sulphite cooking liquor or a pre-hydrolysate portion of cooking liquor or a post-hydrolysate or ultrafiltration permeate thereof.

In the case of the solution to be treated being an aqueous solution of xylose (xylose purity about 30-50%), in accordance with a preferred embodiment of the invention the amount of seed crystals to be used is high, at least 10-fold compared with full seeding. Thus the supersaturation during the crystallization is 1.4-



3.0, preferably 1.5-2.5. The crystal size (length of crystals) obtained is typically 10-100  $\mu\text{m}$ .

A preferred way of carrying out crystallization in accordance with the invention on xylose is cooling of the seeded crystallization mass at a relatively high rate, in a time of about 10-50 hours or less, to the supersaturation value required by nucleation. Herein the temperature of the crystallization mass is typically 20-50  $^{\circ}\text{C}$ , depending on the dry substance content of the crystallization mass, and the viscosity of the crystallization mass is in the range 100-600 Pas.

The suspension is stirred until a sufficient degree of crystallization (yield, decrease in xylose purity of mother liquor) has been reached. For instance, a crystallization vessel equipped with 1.3-1.7 m long (from the shaft to the top) mixer blades with high shear zones is typically utilized at a rotation velocity initially of 3-6 rpm, and at the high viscosity period 0.5-3 rpm. Shear rate relative to intermixing efficiency is controlled to avoid solidification of the crystallization mass while maintaining nucleation. Typically, the power applied to the mixer is between about 100  $\text{W}/\text{m}^3$  and about 800  $\text{W}/\text{m}^3$ . Such a range provides effective mixing whereby the nucleated material is transported to the interior of the crystallization mass. Precipitation period of 1-4 days or even less can reduce (convert to crystalline product) xylose level in the mother liquor to about 20% or less.

Thereafter the supersaturation of the crystallization mass is decreased by increasing the temperature and/or diluting the crystallization mass with water or a xylose-containing solution without significant crystal dissolution until the viscosity of the crystallization mass has decreased to a sufficient degree for effective separation of crystallized matter. A typical viscosity

of the crystallization mass is 5-100 Pas after decreasing the viscosity. The crystals can be separated by filtration, decanting, centrifugation etc., preferably by filtration. The mother liquor (i.e. run-off) thus separated has been reduced to a very low xylose content (as low as 16% on dry substance). The xylose purity of the crystal fraction obtained is typically 60-90% on dry substance, depending on the xylose purity of the crystallization mass and the execution of the process, and said fraction can easily be purified, if necessary, by normal crystallization techniques, for instance. The purity of the crystal fraction obtained by the method of the invention can be improved by displacing a quantity of the mother liquor with a solvent or with air.

It has not been possible to crystallize xylose from solutions having a purity of less than about 70% by the prior art methods without subjecting the solutions to cumbersome purification treatments. The novel method now developed is capable of achieving crystallization with xylose purities as low as about 30% on dry substance.

According to another preferred embodiment of the invention, sucrose can be crystallized from aqueous solutions thereof, such as from molasses obtained in the sugar industry. In this case, a small amount of glycerol (or some other organic solvent that may be present in final molasses) can be added to raw molasses before feeding it to the crystallization process.

The solution thus obtained is evaporated under reduced pressure to a dry substance content (DS) of about 90-95 g/100 g, and the crystallization mass obtained at about 80-90 °C is transferred into a crystallizer.

The crystallization mass is seeded with ground sucrose (mean crystal size from 5 to 10  $\mu\text{m}$ ) at 70-90 °C. Seed crystals are used in an amount that is up to 100-fold compared with the case where the crystallization is based mainly on the growth of crystals. The seed crystal amount is not very essential, since many new crystals are formed by nucleation during effective mixing.

Crystallization is carried out in a crystallizer for about 10 days. The crystallization mass is cooled to about 50 °C in 2-3 days and stirred at that temperature for about 7 days before the preparations for filtration. The viscosity of the crystallization mass is below 800 Pas at its highest, and it decreases as the crystallization proceeds.

Before filtration, the viscosity of the crystallization mass is lowered by increasing the temperature by 5-15 °C and/or optionally adding glycerol and/or water in an amount of up to about 10% by weight. The crystal size obtained is typically about 10-50  $\mu\text{m}$ .

The crystal fraction is preferably recovered by pressure filtration. The effective sucrose yield obtained after filtration in the experiments so far performed has been about 30% of the sucrose contained in the starting molasses having a sucrose purity of 40-60% based on the dry substance content (DS). The yield can be improved by further optimizing the process conditions.

The filtration to recover crystalline product may be conveniently effected with a pressure filter, e.g. Larox filter with 10-20 plates, employing a fiber cloth of moderate porosity, separating at 2-16 bar and 0.5 to 1.0 hour pressing time.

The special embodiments of the method of the invention will be illustrated in greater detail by means of the following examples, which are not intended to limit the scope of the invention.

In some of the examples, the concentration of the crystallizable compound was increased by addition of the pure compound to demonstrate the workability of the invention at different purities.

5           The dry substance contents were determined by the Karl Fischer titration method (DS) or by the refractometric method (RDs).

Carbohydrates were analyzed by liquid chromatography (HPLC) employing columns in which the ion exchange resin was in the Na<sup>+</sup> and Pb<sup>2+</sup> forms, or with PEDLC (i.e., HPLC employing a pulse electrochemical detector). Colour was determined by the adapted ICUMSA method [cf. Sugar Analysis; Official and Tentative Methods Recommended by the International Commission for Uniform Methods of Sugar Analysis (ICUMSA), ed. Schneider, F., ICUMSA, Peterborough, England, 1979, pp. 125-128] at pH 5 (example of xylose crystallization) and pH 7 (other examples) and by performing the measurement from a filtered solution (0.45 µm) at 420 nm.

20           **Example 1**

Crystallization of xylose

150 l of a xylose fraction obtained from a magnesium-base sulphite cooking liquor of beechwood by chromatographic separation (substantially in accordance with the first step of the process described in U.S. Patent 4 631 129), containing about 105 kg of dry substance and having a xylose purity of 39.3%, was evaporated in subatmospheric pressure at about 60 °C to a volume of about 80 l. This xylose fraction was seeded at 25           58 °C with 25 g of ground xylose at a supersaturation value of 2.24, and the crystallization mass was transferred into a 100 l crystallizer.

30           The crystallization mass was subjected to linear cooling from 58 °C to about 20 °C with simultaneous stirring (viscosity 190 Pas measured with a Brookfield vis-

cometer, type RVDV-I+) in about 25 hours, during which time the supersaturation decreased initially to 1.66 in 3.7 hours, thereafter increased to 1.93 (time from seeding 20.9 h, temperature 30.7 °C) and thereafter again gradually decreased (at 20 °C the supersaturation was about 1.70). The crystallization mass was further stirred at about 20 °C. A pressure filter, Larox type PF 0.1 H2, was employed to separate the crystal fraction from the crystallization mass. Samples (à 20-200 g) were taken from the crystallization mass at different times to separate the mother liquor, and stirring of the remainder of the crystallization mass was continued. Prior to the filtration of the crystallization mass, its temperature was increased to about 30 °C to decrease the viscosity.

74.3 hours from the seeding, the viscosity of the sample of crystallization mass was 66 Pas at about 30 °C. The sample of crystallization mass was filtered with the above-mentioned Larox pressure filter, initially using a filtering pressure of 13 bar for 15 minutes, and thereafter a filtering pressure of 14.5 bar for five minutes. The crystal cake obtained had a thickness of about 2.5 cm. The dry substance yield in the crystallization mass prior to filtration was 20.2% and the xylose yield 50.4%. The analysis results are shown in Table 1 below, in which the terms and abbreviations have the following meanings:

Begin = sample of crystallization mass before beginning of cooling

pH 5% = pH determined from sample diluted with water to RDs 5%

Cond. = conductivity determined from sample diluted to RDs 5%

Ash = ash content calculated from conductivity by using sucrose coefficient for sulphate ash

Filtr. = crystallization mass supplied to filter.

The tests carried out showed that the xylose yield and purity were influenced by the stirring time of the crystallization mass in the nucleation zone (in this case, in a temperature range of about 20-30 °C). The xylose purity of the filtered crystal fraction was 83.8% at best (the time from seeding was 76.2 h; the viscosity of the crystallization mass was 66 Pas at 29.8 °C; filtration at 14.5 bar for five minutes), the xylose purity of the filtrate, i.e. run-off, was 18.1% at its lowest (time from seeding 220 h; viscosity of crystallization mass 59 Pas at 29.2 °C; filtration at 13-14 bar for 15 minutes). The xylose yield into crystals of the crystallization mass was 63.2% at its highest (time from seeding 49.3 h).

#### Example 2

##### Crystallization of xylose

Where not otherwise stated, the procedure was similar to that of Example 1. The xylose-containing solution to be treated (20.5 kg) had been obtained by combining a xylose fraction obtained from a magnesium-base sulphite cooking liquor of beechwood by chromatographic separation and an aqueous solution of a crystal cake obtained from previous nucleation crystallization tests. The solution had a dry substance content (DS) of 62.7% and a xylose purity of 53.0%.

The solution was evaporated to a dry substance content (DS) of 89.7%. 13.4 kg of the crystallization mass obtained was transferred into a 10 l crystallizer. Seeding at 65 °C with 5 g of ground xylose (crystal size 50 µm) at a supersaturation of 1.96, and linear cooling from 65 °C to about 20 °C in about 17 hours. During that time, the supersaturation decreased to 1.71, and it remained in the range 1.70-1.76 when the crystallization mass was stirred in the nucleation zone (at a temperature of 20-22 °C). After 21.5 hours from seeding

(viscosity 183 Pas at 22 °C), the crystallization mass was heated to 32 °C and filtered with a pressure filter (15 minutes, filtration pressure 13.5 bar).

5 The dry substance yield into crystals of the crystallization mass prior to filtration was 38.1% and the xylose yield 72.1%. The analysis results are shown in Table 2 below, in which the terms and abbreviations have the same meanings as in Example 1.

### Example 3

#### 10 Crystallization of betaine

The solution to be treated was a run-off obtained by crystallizing betaine from the betaine fraction of chromatographic separation of molasses (cf. the above Finnish Patent 77 845; international application WO 15 81/02420). The dry substance content (DS) of this solution was 63.4 g/100 g, and its analysis results are shown in Table 3 below.

12.3 kg of this solution was evaporated under subatmospheric pressure in a rotating evaporator at a 20 temperature in excess of 80 °C to a dry substance content (DS) of 90.2 g/100 g (the analysis results are shown in Table 3). The linear cooling programme of the concentrated solution thus obtained was started in a 6 l crystallizer from 95 °C, the supersaturation of the solution 25 then being 1.74. During the entire crystallization, the crystallization mass was vigorously stirred. After 6.2 hours, the temperature was 76.5 °C, the supersaturation was 3.18, and no crystallization had taken place. At that point, 0.6 g of ground betaine monohydrate was 30 added, and nucleation started. Samples (à 20-200 g) were taken from the crystallization mass at different times to separate the mother liquor, and stirring of the crystallization mass was continued. The cooling was continued linearly to 30 °C (time from seeding with betaine 35 monohydrate 31.1 h), the supersaturation then being

2.43. The crystallization mass was stirred at this temperature for 3.8 hours, whereafter the temperature was raised to 35 °C in 0.8 hours (the viscosity was then 113 Pas) and further to 37 °C in 0.9 hours. At that point, the viscosity was 84 Pas, and the crystal fraction was separated from the crystallization mass with the Larox pressure filter of Example 1 employing a filtration pressure of 14-15 bar for 30 minutes. A dry crystal cake having a thickness of 8 mm was obtained.

The analysis results are shown in Table 3 below, in which the terms and abbreviations have the same meanings as in the previous examples, except that the colour has been measured at pH 7. Furthermore, the term "Solution" employed in the first column refers to the raw material solution prior to evaporation.

The betaine yield into the crystal fraction was 37.7% of the betaine contained in the original solution, and the inositol yield into the crystal fraction was 55.5% of the inositol contained in the solution.

The tests carried out showed that the betaine and inositol yield and purity were influenced by the stirring time of the crystallization mass in the nucleation zone. The combined betaine and inositol purity of the filtered crystal fraction was 87.1% at best (the time from seeding was 37 h). The betaine purity of the filtrate, i.e. run-off, separated from the crystal mass was 33.3% at its lowest and the inositol purity was 7.0 (time from seeding 31 h).

#### Example 4

##### Crystallization of betaine

The solution to be treated was that of Example 3. 13.6 kg of this solution was evaporated under subatmospheric pressure in a rotating evaporator at a temperature slightly below 80 °C to a dry substance content (DS) of 97.6 g/100 g. In that situation, seeding was



spontaneous, the supersaturation being 3.69. 7 kg of crystallization mass was transferred into a 6 l crystallizer to 95 °C, and 150 ml of water at about 90 °C was added thereto. The crystallization mass thus prepared was cooled down linearly by vigorous stirring in 10 hours from 95 °C to 70 °C. The crystallization mass was stirred at this temperature for about nine hours (overnight), whereafter it was cooled for about five hours to a constant temperature of 36 °C, at which it was stirred for about 62 hours. The viscosity of the crystallization mass was 15.6 Pas at 70 °C, 55 Pas at 45 °C, and after stirring of 90 hours (from seeding) 347 Pas at 36 °C. After the above stirring time, the temperature of the crystallization mass was first raised to 48 °C (viscosity 75 Pas), and thereafter the crystal fraction was separated from the crystallization mass at 45 °C (viscosity 116 Pas, supersaturation 17.87) with the Larox pressure filter of Example 1 employing a filtration pressure of 14.5 bar for 30 minutes. A sufficiently dry crystal cake having a thickness of 8 mm was obtained.

The analysis results are shown in Table 4 below, in which the terms and abbreviations correspond to those of Example 3.

The betaine yield into the crystal fraction was 47.0% of the betaine contained in the original solution, and the inositol yield was 60.5% of the inositol contained in the solution.

The combined betaine and inositol purity of the filtered crystal fraction was 77.3% at best, and the betaine purity of the run-off was 30.9% at its lowest and the inositol purity was 6.5% at its lowest.

### Example 5

#### Crystallization of xylitol

The solution to be treated was a run-off obtained from the crystallization of xylitol. It was evaporated with a rotating evaporator at a pressure of 40 mbar at 70 °C to a dry substance content (RDs determined by reading tables of xylitol) of 93.8 g/100 g.

12.3 kg of the obtained crystallization mass was transferred into a 10 l crystallizer to a temperature of 50 °C ( $s = 1.5$ ), seeded with 10 g of ground xylitol, and cooled down to 25 °C in 10 hours. About three hours after the temperature of 25 °C had been reached, the crystallization mass had a viscosity of 61.5 Pas ( $s = 3.9$ ). The crystallization mass was stirred at this temperature for a total of 8 hours, whereafter the temperature was further lowered (temperature of cooling water 15 °C). After about three hours, the crystallization mass had a temperature of 16 °C ( $s = 4.9$ ). The crystallization mass was stirred at this bath temperature for 18 hours, whereafter the viscosity was 250 Pas ( $s = 3.0$ ) when the crystallization mass had a temperature of 18 °C.

Thereafter the temperature of the crystallization mass was raised to 25 °C in about three hours (the viscosity was then 81.5 Pas ( $s = 2.1$ )) and further to 28 °C in about two hours.

At that point, the crystallization mass had a viscosity of 59.5 Pas ( $s = 2.0$ ), and the crystal fraction was separated from the crystallization mass with the Larox pressure filter of the previous examples employing a filtration pressure of 12 bar for 15 minutes. The compression was removed before a proper crystal cake had been formed.

The analysis results are shown in Table 5 below, in which the terms and abbreviations have the same meanings as in Example 3.

The xylitol yield into the crystal fraction was 67% of the xylitol contained in the initial solution.

#### Example 6

##### Crystallization of sucrose

5 The solution to be treated was molasses obtained from a beet sugar factory. The solution was evaporated in a rotating evaporator to a dry substance content (RDs determined by reading tables of sucrose) of 90.3 g/100 g.

10 14.5 kg of the crystallization mass obtained was transferred into a 10 l crystallizer to a temperature of 62 °C and seeded with 10 g of ground sucrose, and cooled down with simultaneous vigorous stirring to 40 °C in 40 hours. About 25 hours after the temperature of 40 °C had  
15 been reached, the crystallization mass had a viscosity of 550 Pas. The temperature of the crystallization mass was raised to 53 °C in about five hours, the viscosity then being 111 Pas, and the crystal fraction was separated with a Larox pressure filter employing a filtration  
20 pressure of 12 bar for 15 minutes. The compression was removed before a sufficiently dry crystal fraction had been formed.

The analysis results are shown in Table 6 below, in which the terms and abbreviations have the same meanings as in Example 3.  
25

#### Example 7

##### Crystallization of xylitol

The starting material was a run-off obtained from previous crystallizations of xylitol. It was filtered by  
30 a laboratory vacuum filter. The purity of xylitol on dry substance basis (RDs) in the obtained solution was increased to about 46% by adding pure crystalline xylitol. The solution was evaporated with a laboratory vacuum evaporator at a bath temperature of 60-70 °C  
35 during 6 hours to a dry substance content (RDs) of 94.1 g/100 g.

13.58 kg (a volume of 10 l) of the crystallization mass thus obtained was transferred into a 10 l crystallizer to a bath temperature of 50 °C and stirred for twenty minutes. At that time, the crystallization mass had a temperature of 51 °C and the supersaturation was 1.7. The crystallization mass was then seeded with 10 g of ground xylitol and subjected to linear cooling from 50 °C to 23 °C (temperature of cooling water) within 15 hours. At the end of this cooling period, the crystallization mass had a temperature of 24 °C, a viscosity of 110 Pas, and a supersaturation of 3.2.

The crystallization mass was further stirred at this temperature for about 2 hours, whereafter its temperature was lowered to 20 °C during about 3 hours (the viscosity was then 200 Pas; supersaturation 3.5) and further to 16 °C during about 3 hours. The crystallization mass then had a viscosity of 345 Pas. Stirring of the crystallization mass at approximately this temperature (cooling water at a constant temperature of 15 °C) was continued for 42 hours. A sample taken after 17 hours stirring at this temperature had a viscosity of 400 Pas and a supersaturation of 4.0. At the end of this stirring period, the viscosity of the crystallization mass was 407 Pas.

Thereafter the temperature of the crystallization mass was raised to 20 °C in half an hour (the viscosity was then 256 Pas) and further to 23 °C in three hours. At that point, the crystallization mass had a viscosity of 198 Pas. A sample of the crystallization mass was taken at this point, and a run-off sample was separated therefrom by a laboratory centrifuge.

The crystallization mass was then removed from the crystallizer, water was added in an amount of 5% by weight of the crystallization mass to lower the viscosity, and the crystal fraction was separated with

the Larox pressure filter of the previous examples employing a filtration pressure of 15 bar for 30 minutes.

The analysis results are shown in Table 7 below, in which the terms and abbreviations have the same meanings as in Example 5.

The xylitol yield into the crystal cake during the Larox filtration was 57% of the xylitol contained in the initial solution.

#### Example 8

##### Crystallization of xylitol

The same starting material was used as in Example 7. The purity of xylitol in the filtered solution was increased to about 47% by adding pure crystalline xylitol. The solution was evaporated with a rotating evaporator at a bath temperature of 70 °C to a dry substance content (RDs) of 94.4 g/100 g.

13.52 kg of the crystallization mass thus obtained was transferred into a 10 l crystallizer. As in Example 7, the crystallization mass was effectively stirred during the entire procedure. The crystallization mass was seeded at a temperature of 56 °C ( $s = 1.4$ ) with 10 g of ground xylitol and subjected to linear cooling. In approximately 26 hours, the crystallization mass had reached a temperature of 20.5 °C. The crystallization mass was stirred at this temperature for 42 hours, after which time the supersaturation was 3.6. The viscosity of the crystallization mass at the end of this stirring period was 280 Pas.

Thereafter, the temperature of the crystallization mass was raised to 25 °C in about two hours (the viscosity was then 176 Pas;  $s = 3.1$ ) and stirring at this temperature was continued for one hour. A sample of the crystallization mass was taken at this point, and a run-off sample was separated therefrom by a laboratory centrifuge.

Part of the crystallization mass was then removed from the crystallizer, and water was added thereto in an amount of 5% by weight to lower the viscosity, which was 28 Pas after the addition of water. The crystal fraction was separated from this part with the Larox pressure filter of the previous examples employing a filtration pressure of 16 bar for 1 h 15 min.

Ethanol was added to the remainder of the crystallization mass in the crystallizer in an amount of 5% by weight of the crystallization mass, which was stirred at 25 °C for about half an hour. The crystallization mass was then removed from the crystallizer and filtered in the same way as described above for the first part of the crystallization mass.

The analysis results are shown in Table 8 below, in which the terms and abbreviations have the same meanings as in Example 5, Filtration I refers to the Larox filtration with an addition of water, and Filtration II to the Larox filtration with an addition of ethanol.

The xylitol yield into the crystal cake from the first filtration (with the addition of water) was 68% and from the second filtration (with the addition of ethanol) 74% of the xylitol contained in the initial solution.

#### Example 9

##### Crystallization of sucrose

The raw material to be treated was molasses obtained from a beet sugar factory. The molasses was filtered and the filtrate evaporated under reduced pressure to a dry substance content of Bx 93.0.

100 l of the crystallization mass obtained was transferred into a 100 l crystallizer, seeded with 100 g of ground sucrose at 78.5 °C and cooled down with simultaneous effective stirring to 50 °C in about 60 hours. The viscosity of the crystallization mass was

then about 800 Pas, and stirring was continued keeping the temperature substantially unchanged. About 170 hours after the temperature of 50 °C had been reached, the crystallization mass had a viscosity of about 670 Pas. After 172 hours at about 50 °C, the temperature of the crystallization mass was raised to about 60 °C in about five hours, and after about 24 hours at this temperature, the crystallization mass had a viscosity of about 280 Pas. About 60 hours after reaching the temperature of 60 °C, the crystallization mass had a viscosity of 241 Pas.

The viscosity was further lowered by an addition of water (2% by weight), and the crystal fraction was separated with a Larox pressure filter employing a filtration pressure of 16 bar for 60 minutes. The temperature of the Larox feed (filtr.) was rapidly raised to 69 °C just before filtration.

The analysis results are shown in Table 9 below, in which the terms and abbreviations have the same meanings as in the preceding examples, unless otherwise indicated.

#### Example 10

##### Crystallization of sucrose

The raw material to be treated was the same molasses as in Example 9, and it was initially treated as described in Example 9, except that some glycerol fraction was added to the filtered solution before evaporation. A glycerol fraction obtained from a chromatographic fractionation of vinasse was used for the glycerol addition, and the added amount of glycerol was 10% of the dry substance contained in the filtered solution.

A 100 l crystallizer was charged with the crystallization mass thus obtained (Bx 92.0), and the crystallization mass was seeded with 100 g of ground

sucrose at 76 °C. The crystallization mass was cooled down with simultaneous effective stirring to about 50 °C in about 60 hours. The viscosity of the crystallization mass was then about 210 Pas, and stirring was continued at this temperature for 11 hours. Thereafter, the temperature was lowered to 46.5 °C, whereby the viscosity first increased to about 280 Pas and gradually decreased to about 220 Pas in 145 hours at this temperature.

The temperature was then gradually raised to 53 °C (viscosity 120 Pas) and after about 30 hours at this temperature, the crystal fraction was separated with a Larox pressure filter employing a filtration pressure of 16.2 bar for 65 minutes.

The analysis results are shown in Table 10 below, in which the terms and abbreviations have the same meanings as in the preceding examples.

Sucrose yield to the crystal cake during the Larox filtration was 35% from the sucrose of the original feed syrup.

#### Example 11

##### Crystallization of sucrose

The raw material to be treated was molasses obtained from a cane sugar factory. The molasses was evaporated under reduced pressure to a dry substance content of DS 88.1 (determined by Karl-Fisher method).

12.3 kg of the crystallization mass obtained was transferred into a 10 l crystallizer, seeded with 10 g of ground sucrose at about 75 °C and cooled down with simultaneous effective stirring to 50 °C in about 60 hours. The viscosity of the crystallization mass was then about 860 Pas, and stirring was continued keeping the temperature substantially unchanged. Eleven days after the temperature of 50 °C had been reached, the crystallization mass had a viscosity of about 800 Pas, first run-off sample was separated from the crystalliza-



tion mass with a laboratory centrifuge, and 50 ml water was mixed into the mass to reduce viscosity.

Four days after the water addition, the crystallization mass had a viscosity of about 510 Pas and temperature 50 °C, second run-off sample was separated from the crystallization mass with a laboratory centrifuge, and 200 ml water was mixed into the mass to reduce viscosity.

Four days after the 200 ml water addition, the viscosity was further lowered by raising the temperature of the crystallization mass to about 60 °C in about five hours. After about an hour at this temperature, the crystallization mass had a viscosity of about 75 Pas and a crystal fraction was separated with a Larox pressure filter employing a filtration pressure of 16 bar for 60 minutes. Filtration rate was slow. The filter cloth was Tamfelt 71-2209-L1 with pore size about 17 micrometer.

The analysis results are shown in Table 11 below, in which the terms and abbreviations have the same meanings as in the preceding examples, unless otherwise indicated.

#### Example 12

##### Crystallization of sucrose

The raw material to be treated was the same molasses as in Example 11, except that some sucrose was added before evaporation to rise the purity of the feed syrup to about 58%/DS. The syrup was evaporated under reduced pressure to a dry substance content of DS 89.7.

8.4 kg of the crystallization mass obtained was transferred into a 6 l crystallizer, seeded with 8 g of ground sucrose at about 75 °C and cooled down with simultaneous effective stirring to 50 °C in about 60 hours. The viscosity of the crystallization mass was then about 900 Pas, and 60 ml water was mixed into the mass to reduce viscosity, and stirring was continued

keeping the temperature substantially unchanged. Eight days after the temperature of 50 °C had been reached, the crystallization mass had a viscosity of about 720 Pas, first run-off sample was separated from the crystallization mass with a laboratory centrifuge, and 20 ml water was mixed into the mass.

Four days after the water addition, the crystallization mass had a viscosity of about 610 Pas and temperature 50 °C, and 1 kg of a 63% glyserol/water solution was mixed into the mass to reduce viscosity.

Five days after the glyserol addition, the viscosity of the crystallization mass was 17 Pas and temperature 50 °C. After one day mixing at this temperature, a crystal fraction was separated with a Larox pressure filter employing a filtration pressure of 16 bar for 60 minutes. The filter cloth was same than in the Example 11.

The analysis results are shown in Table 12 below, in which the terms and abbreviations have the same meanings as in the preceding examples, unless otherwise indicated.

Sucrose yield to the crystal cake during the Larox filtration was about 45% from the sucrose of the feed syrup.

The yields of dry substance (expressed in w/w%) given in the above examples are calculated using the following formula:

$$\text{Yield of dry substance} = \left( \text{Yield of crystallizable compound} \right) \times \left( \frac{Q_{\text{mass}}}{Q_{\text{crystal}}} \right)$$

wherein  $Q_{\text{mass}}$  is the purity of the crystallization mass and  $Q_{\text{crystal}}$  is the purity of the crystal cake.

The yields obtained in Examples 1-12 as well as feed purity in each case, i.e. the concentration of the compound to be recovered in the feed on dry substance basis, are summarized in Table 13 below.

5 In Table 13, total (i.e. true) yields of filtration are calculated from the crystallization mass, filtration run-off and crystal cake purities using the following formula:

$$10 \quad \begin{array}{l} \text{Total yield of} \\ \text{filtration} \end{array} = \left( \frac{Q_{\text{mass}} - Q_{\text{run-off}}}{Q_{\text{crystal}} - Q_{\text{run-off}}} \right) \times \left( \frac{Q_{\text{crystal}}}{Q_{\text{mass}}} \right) \times 100\%$$

15 wherein  $Q_{\text{mass}}$  and  $Q_{\text{crystal}}$  are as defined above, and  $Q_{\text{run-off}}$  is the purity of the filtration run-off.

For example, the yield of xylose in Example 1, using the data from Table 1, is calculated as follows:

$$20 \quad \begin{array}{l} \text{Yield of} \\ \text{xylose} \end{array} = \frac{40.1 - 22.4}{74.5 - 22.4} \times \frac{74.5}{40.1} \times 100\%$$

$$= 63.1\%$$

25 The effective yields of filtration are calculated with 100% crystal cake purity. These tell how much pure compound can be refined from the low purity crystal cake.

Table 1

## Analysis of xylose crystallization

	Begin	Filtr.	Crystal cake	Run-off
Dry substance content (DS), g/100 g	89.2	88.0	93.3	79.2
pH (solution 30-50%)	2.5	2.6	2.6	2.6
pH 5%	2.9	2.9	3.0	3.0
Cond. (from solution having 5% of dry substances), mS/cm	2.22	2.20	1.16	2.64
Ash, %	3.99	3.96	2.08	4.39
Colour, ICUMSA	14000	15000	6800	19600
Carbohydrate content, % on dry substance (DS)				33
glucose	2.7	2.6	1.8	3.2
xylose	40.1	40.5	74.5	22.4
galact. + rhamn.	3.7	3.8	1.8	4.6
arabinose	0	0	0	0
mannose	3.6	0.7	0.3	4.5

Table 2

## Analysis of xylose crystallization

	Begin	Filtr.	Crystal cake	Run-off
Dry substance content (DS), g/100 g	89.7	89.9	94.8	83.7
pH 5%	3.1	3.1	3.2	3.0
Cond. (from solution having 5% of dry substances), mS/cm	2.22	2.22	1.23	3.02
Ash, %	4.00	4.00	2.22	5.44
Colour, ICUMSA	13000	13400	700	20000
Carbohydrate content, % on dry substance (DS)				
glucose	2.2	2.3	1.2	3.1
xylose	52.5	52.8	78.0	29.2
galact. + rhamn.	3.2	3.2	1.5	4.3
arabinose	0	0	0	0
mannose	2.6	2.6	1.23	3.8

Table 3

## Analysis of betaine crystallization

	Solution	Begin	Filtr.	Crystal cake	Run-off
Dry substance content (DS), g/100 g	63.4	90.2	91.9	91.1	89.8
pH (solution 30-50%)	9.9	10.0	10.0	10.0	10.0
pH 5%	9.8	9.8	9.8	9.6	9.7
Cond. (from solution having 5% of dry substances), mS/cm	2.50	2.49	2.49	1.00	3.00
Ash, %	4.50	4.48	4.48	1.81	5.40
Colour, ICUMSA	127500	139400	132500	42400	165000
Carbohydrate content, % on dry substance (DS)					35
raffinose	0.1	0.0	0.0	0.0	0.0
sucrose	1.8	1.8	1.8	0.7	2.2
other disaccharides	0.5	0.7	0.7	0.0	0.4
glucose	5.4	5.5	5.6	1.7	6.6
fructose	7.9	7.9	8.3	2.7	9.7
inositol	11.1	11.2	11.2	21.6	7.0
glycerol	8.1	8.3	8.8	3.5	9.7
betaine	46.8	47.4	47.3	65.5	40.5

Table 4

## Analysis of betaine crystallization

	Begin	Filtr.	Crystal cake	Run-off
Dry substance content (DS), g/100 g	97.6	95.5	96.9	93.6
pH 5%	9.9	9.9	9.7	9.9
Cond. (from solution having 5% of dry substances), mS/cm	2.50	2.54	1.32	3.34
Ash, %	4.50	4.57	2.38	6.01
Colour, ICUMSA	130000	135000	30900	183000
Carbohydrate content, % on dry substance (DS)				
raffinose	0.0	0.0	0.0	0.0
sucrose	1.6	1.7	0.7	2.3
other disaccharides	0.4	0.0	0.0	0.6
glucose	5.8	6.2	2.3	8.2
fructose	7.6	9.3	3.6	11.6
inositol	10.4	11.6	17.1	6.5
glycerol	7.0	7.7	3.3	9.7
betaine	43.6	48.9	60.2	35.1

Table 5

## Analysis of xylitol crystallization

	Begin	Filtr.	Crystal cake	Run-off <sup>1)</sup>
Dry substance content (RDs), g/100 g	93.8	92.9	92.5	17.2 <sup>2)</sup>
Carbohydrate content, % on dry substance (RDs)				
monosaccharides	4.4	4.5	3.5	5.8
glycerol	4.0	4.1	3.4	4.8
mannitol	12.0	12.0	10.7	14.3
rhamnitol	0.9	0.9	0.9	1.1
xylitol	38.0	38.1	44.12	29.7
sorbitol	8.5	7.6	7.8	9.8
others (undetected substance)	32.2	32.9	29.6	34.5

37

<sup>1)</sup> The run-off sample was separated from the crystallization mass supplied to the filter with a laboratory centrifuge (4500 rpm).

<sup>2)</sup> The sample was diluted with water, and the initial dry substance content was not determined.



Table 6

## Analysis of sucrose crystallization

	Begin	Filtr.	Run-off	Run-off <sup>2)</sup>	
Dry substance content (RDs), g/100 g	90.3	91.0	81.9	-	
Carbohydrate content, % on dry substance (RDs)					
raffinose	2.2	2.2	2.3	2.3	38
sucrose	60.0	57.8	55.1	54.0	
betaine	5.6	5.9	6.2	6.4	

<sup>2)</sup> The run-off sample was separated by filtration from the crystallization mass with a laboratory centrifuge (4500 rpm).

Table 7

## Analysis of xylitol crystallization

	End	Filtr.	Crystal cake	Run-off <sup>1)</sup>	Run-off <sup>2)</sup>
Dry substance content (RDs), g/100 g	93.9	89.4	94.3	77.7	-
Carbohydrate content, % on dry substance (RDs)					
glycerol	5.1	4.2	2.3	5.3	6.3
mannitol	10.8	10.2	5.5	14.4	16.8
rhamnitol	0.9	0.9	0.4	1.3	1.4
xylitol	45.4	46.3	71.8	30.4	23.1
sorbitol	7.0	7.8	4.6	10.2	11.6
others (monosaccharides and undetected substance)	30.8	30.6	15.1	38.4	42.2

39

End = crystallization mass in the end of the crystallization

<sup>1)</sup> The run-off from the Larox pressure filter

<sup>2)</sup> The run-off sample separated from the crystallization mass with a laboratory centrifuge (4500 rpm).

Table 8

## Analysis of xylitol crystallization

Carbohydrate content, & on dry substance (RDs)	Begin	Filtr.	Crystal cake	Run-Off <sup>1)</sup>	Run-off <sup>2)</sup>
<u>Filtration I</u>					
Dry substance content					
(RDs), g/100 g	94.0	89.9	94.2	82.4	-
glycerol	2.1	3.7	3.0	3.4	2.3
mannitol	8.7	9.4	4.3	13.4	15.1
rhamnitol	0.7	0.5	1.1	0.7	0.9
xylitol	49.5	46.7	75.2	28.4	22.9
sorbitol	5.2	7.4	10.1	10.4	10.6
others (monosaccharides and undetected substance)	33.8	32.3	6.3	43.7	48.2
					40
<u>Filtration II</u>					
Dry substance content					
(RDs), g/100 g	94.0	89.0	94.7	79.5	-
glycerol	2.1	3.3	-	-	-
mannitol	9.7	9.1	4.1	12.6	-
rhamnitol	0.7	0.5	0.0	0.8	-
xylitol	49.5	45.2	74.5	24.9	-
sorbitol	5.2	7.2	3.5	9.5	-
others (monosaccharides and undetected substance)	32.8	34.7	17.9	52.2	-

<sup>1)</sup> The run-off sample from the Larox pressure filter

<sup>2)</sup> The run-off sample separated from the crystallization mass with a laboratory centrifuge (4500 rpm).

Table 9

## Analysis of sucrose crystallization

	Feed syrup	Begin	Filtr.	Crystal cake	Run-off <sup>1)</sup>
Dry substance content Brix	77.0	92.7	90.8	93.6	-
Carbohydrate content, & on dry substance (RDs)					
raffinose	2.5	2.6	3.5	1.8	3.7
sucrose	60.9	61.5	61.0	70.8	52.9
betaine	5.2	5.3	5.4	3.2	5.8

41

<sup>1)</sup> The run-off sample separated from the crystallization mass with a laboratory centrifuge (4500 rpm).

Table 10

## Analysis of sucrose crystallization

	Begin	Filtr.	Crystal cake	Run-Off <sup>1)</sup>	Run-Off <sup>2)</sup>
Dry substance content Brix	92.0	92.2	95.2	90.0	-
Carbohydrate content, % on dry substance. (RDs)					
raffinose	2.6	2.6	1.1	3.2	3.1
sucrose	54.8	52.2	80.5	46.7	44.1
glucose	2.8	2.8	1.9	3.2	3.2
fructose	0.6	0.5	0.9	0.5	0.6
inositol	0.4	0.3	0.1	0.3	0.4
glycerol	8.3	8.2	2.9	9.8	9.5
betaine	5.1	5.0	1.8	6.1	5.8

<sup>1)</sup> The run-off from the Larox pressure filter

<sup>2)</sup> The run-off sample separated from the crystallization mass with a laboratory centrifuge (4500 rpm).

Table 11

## Analysis of sucrose crystallization

	Begin	1st Run-off <sup>1)</sup>	2nd Run-off <sup>1)</sup>	Run-off <sup>2)</sup>
Dry substance content (DS), g/100 g	88.1	39.6 <sup>3)</sup>	45.7 <sup>3)</sup>	25.7 <sup>3)</sup>
Carbohydrate content, % on dry substance (DS)				
raffinose	1.2	1.4	1.3	1.4
sucrose	43.0	36.0	38.8	41.4
glucose	3.6	2.2	2.2	2.1
fructose				

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<sup>1)</sup> The run-off sample separated from the crystallization mass with a laboratory centrifuge (4500 rpm)

<sup>2)</sup> The run-off from the Larox pressure filter

<sup>3)</sup> The DS is measured after dilution of the sample.

Table 12

## Analysis of sucrose crystallization

	Begin	Filtr.	Crystal cake	Run-off <sup>1)</sup>	1st Run-off <sup>2)</sup>
Dry substance content (DS), g/100 g	89.7	86.3	45.5 <sup>3)</sup>	34.5 <sup>3)</sup>	47.9 <sup>3)</sup>
Carbohydrate content, % on dry substance (DS)					
raffinose	1.0	1.1	0.6	1.1	1.4
sucrose	57.3	50.2	66.3	41.8	37.5
glucose	2.7	1.5	1.0	1.9	2.3
fructose	6.3	5.3	3.2	0.3	7.1
glycerol	0	11.7	7.2	13.4	0

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<sup>1)</sup> The run-off from the Larox pressure filter

<sup>2)</sup> The run-off sample separated from the crystallization mass with a laboratory centrifuge (4500 rpm)

<sup>3)</sup> The DS is measured after dilution of the sample.

Table 13

Example	Feed purity	Total yield of filtration	Effective yield of filtration
1	40%	xylose 63-76%	57-67%
2	52.5%	xylose 71%	63%
3	11.2% 47.3%	inositol betaine 55% 38%	40% 24%
4	10.4% 43.6%	inositol betaine 60.5% 47%	40% 30%
5	38%	xylitol 67%	31%
6	60%	sucrose -	18%
7	45.4%	xylitol 57%	47%
8	49.5%	xylitol 68%	60%
9	61%	sucrose 52%	28%
10	55%	sucrose 35%	28%
11	43%	sucrose -	25%
12	57.3%	sucrose 45%	29%



## Claims:

1. A method for recovering a crystallisable organic compound from solutions containing said compound, characterized in that the compound is crystallized substantially by way of nucleation from a solution having high viscosity and high supersaturation in respect of the compound to be recovered, and the formed crystals are recovered.
2. A method as claimed in claim 1, characterized in that the solution is brought to a supersaturated state by evaporating and a high viscosity is achieved by cooling.
3. A method as claimed in claim 2, characterized in that the cooling is carried out during 10-100 hours.
4. A method as claimed in claim 3, characterized in that the cooling is carried out in the temperature range 95-20 °C.
5. A method as claimed in any one of claims 1-4, characterized in that nucleation is effected in a supersaturated solution having high viscosity by effective stirring.
6. A method as claimed in any one of claims 1-5, characterized in that to initiate nucleation, seed crystals of the compound to be recovered are added to the supersaturated solution during evaporation or cooling.
7. A method as claimed in claim 6, characterized in that seed crystals are employed in an amount at least 10-fold in relation to full seeding.
8. A method as claimed in any one of claims 1-7, characterized in that the viscosity of the suspension containing the supersaturated solution and crystals of the compound to be recovered is reduced immediately prior to the recovery of crystals.

9. A method as claimed in claim 8, characterized in that the viscosity is reduced by heating and/or diluting the suspension.

5 10. A method as claimed in claim 8, characterized in that the viscosity is reduced by diluting the suspension with a solvent without significant dissolution of the crystals.

10 11. A method as claimed in claim 8, characterized in that the viscosity is reduced by mixing steam into the suspension.

12. A method as claimed in any one of claims 1-11, characterized in that the crystals are recovered by filtration.

15 13. A method as claimed in claim 12, characterized in that the crystals are recovered by pressure filtration.

20 14. A method as claimed in any one of claims 1-13, characterized in that the solution to be treated is an aqueous solution of the organic compound to be recovered.

25 15. A method as claimed in any one of claims 1-14, characterized in that the organic compound to be recovered is a sugar, a sugar alcohol or other polyol, or a sugar alcohol anhydride.

30 16. A method as claimed in any one of claims 1-14, characterized in that the organic compound to be recovered is a carbohydrate, hydroxy acid or a salt thereof or an amino acid or a salt thereof.

35 17. A method as claimed in claim 14 or claim 15, characterized in that the organic compound to be recovered has been selected from xylose, mannose, xylitol, mannitol, lactose, lactitol, sucrose, glucose, fructose, maltose, maltitol, isomaltose, isomaltulose, lactulose,  $\alpha$ -D-glucopyranocyl(1-6)mannitol,  $\alpha$ -D-glucopyranocyl(1-6)sorbitol,  $\beta$ -cyclodextrin, itaconic acid,

citric acid, inositol, lactic acid, 1,4-anhydroglucitol, gluconates and glutamates.

18. A method as claimed in claim 17, c h a r -  
a c t e r i z e d in that the organic compound to be  
5 recovered is xylose.

19. A method as claimed in claim 18, c h a r -  
a c t e r i z e d in that the supersaturation of the  
solution in respect of xylose during crystallization is  
in the range 1.4-4.0.

20. A method as claimed in claim 18 or claim 19,  
10 c h a r a c t e r i z e d in that the viscosity of the  
supersaturated solution during nucleation is in the  
range from about 100 to about 1000 Pas.

21. A method as claimed in claim 20, c h a r -  
15 a c t e r i z e d in that the viscosity of the suspen-  
sion is reduced prior to the recovery of crystals to be  
in the range 5-100 Pas.

22. A method as claimed in claim 17, c h a r -  
a c t e r i z e d in that the organic compound to be  
20 recovered is xylitol.

23. A method as claimed in claim 17, c h a r -  
a c t e r i z e d in that the organic compound to be  
recovered is sucrose.

24. A method as claimed in any one of claims 1-  
25 14, c h a r a c t e r i z e d in that the organic com-  
pound to be recovered is betaine.

25. A method as claimed in claim 18, 22, 23 or  
24, c h a r a c t e r i z e d in that the supersatur-  
ation of the solution in respect of the substance to be  
30 recovered during crystallization is in excess of 1.3.

26. A method as claimed in claim 25, c h a r -  
a c t e r i z e d in that the viscosity of the super-  
saturated solution during nucleation is in excess of 100  
Pas.

27. A method as claimed in claim 26, c h a r -  
a c t e r i z e d in that the viscosity is reduced to  
have a value below 100 Pas prior to the recovery of  
crystals.

5 28. A method as claimed in any one of claims 25-  
27, c h a r a c t e r i z e d in that the cooling time  
is less than 100 hours.

29. A method as claimed in any one of claims 25-  
28, c h a r a c t e r i z e d in that the total time  
10 to the start of crystal separation is less than 300  
hours.

30. A method as claimed in any one of claims 1-  
29, c h a r a c t e r i z e d in that the solution  
containing an organic compound is a biomass-derived  
15 aqueous solution or a fermentation solution.

31. A method as claimed in claim 30, c h a r -  
a c t e r i z e d in that the biomass-derived aqueous  
solution has been selected from molasses, vinasse, bio-  
mass hydrolysate and parts thereof and concentrates  
20 obtained therefrom.

32. A method as claimed in any one of claims 1-  
31, c h a r a c t e r i z e d in that the run-off  
separated in the recovery of crystals is used to prepare  
a new supersaturated solution for crystallization based  
25 predominantly on nucleation.

33. A method as claimed in any one of claims 1-  
32, c h a r a c t e r i z e d in that the crystals  
obtained are recrystallized by repeating said method or  
in a manner known per se.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 96/00124

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C13K 13/00, C13F 1/02, B01D 9/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C13K, C13F, B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC, CAPLUS, JAPIO

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Warren L. McCabe et al: "Unit operations of chemical engineering", second edition, 1967, McGraw-hill book company, New York, see pages 756-764	1-33
X	GB 1342126 A (BATTELLE DEVELOPMENT CORPORATION), 28 December 1973 (28.12.73), page 2, line 16 - line 49	1-33

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

4 June 1996

Date of mailing of the international search report

12-06-1996

Name and mailing address of the ISA /

Authorized officer

01/04/96

PCT/FI 96/00124

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB-A-	1342126	28/12/73	AU-B-	452905	19/09/74
			AU-A-	3181871	01/02/73
			US-A-	3695932	03/10/72